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<p>(54) Title: HAIR CARE COMPOSITIONS COMPRISING OPTICAL BRIGHTENERS AND SILICONE COMPOUNDS</p> <p>(57) Abstract</p> <p>Disclosed are hair care compositions comprising: (a) an effective amount of an optical brightener selected from the group consisting of polystyrylstilbenes, hydroxycoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof; and (b) a silicone compound. Further disclosed are shampoo compositions comprising: (a) an effective amount of an optical brightener; (b) a detergentsurfactant suitable for cleansing the hair; and (c) a silicone compound.</p>			

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# HAIR CARE COMPOSITIONS COMPRISING OPTICAL BRIGHTENERS AND SILICONE COMPOUNDS

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## TECHNICAL FIELD

The present invention relates to a hair care composition comprising optical brighteners which alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage. More specifically, the present invention relates to a hair care composition comprising optical brighteners and silicone compounds.

## BACKGROUND

The desire to regain the natural color and shine of damaged hair and the desire to alter the color of the hair to be more appealing are widely held. Damaged hair is perceived by the consumer as unfavorable appearances and less manageability of the hair. Such unfavorable appearances include alteration and fading of original color, less shine, and less luster.

A common way for alleviating the unfavorable appearances of damaged hair and to achieve appealing hair color is to dye the hair to the color desired. Dyeing the hair would provide the consumer with a stable color of hair for a relatively long period. However, dyeing the hair is generally time-consuming, cumbersome, and messy. Dyestuff may also be chemically harsh to the hair, scalp, and skin. The hair can be further damaged by dyeing. Thus, hair dye products are not suitable for daily use. Further, dyeing can leave the hair with a dull appearance, making the hair look less shiny.

Based on the foregoing, there is a need for a hair composition which can be used daily and which can alter the color of the hair, while enhancing the shininess of the hair, and protecting the hair from further damage.

35 Use of optical brighteners, or compounds otherwise described by names such as fluorescent whitening agents, fluorescent brighteners, or fluorescent

dyes, in the hair care field has been known in the art, such as in United States Patent 3,658,985, United States Patent 4,312,855, Canadian Patent 1,255,603, United States Patent 3,577,528, Great Britain Patent Specification 1,328,108, South African Application 676,049, European Publication 87,060, and Great Britain Patent Specification 2,307,639.

However, the use of optical brighteners alone may not provide sufficient conditioning benefits such as combing and smoothness. Thus there is also a need for a hair care compositions comprising optical brighteners and providing conditioning benefits.

None of the existing art provides all of the advantages and benefits of the present invention.

### SUMMARY

The present invention is directed to a hair care composition comprising:  
15 (a) an effective amount of an optical brightener selected from the group consisting of polystyrylstilbenes, hydroxycoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof; and (b) a silicone compound. The present invention is further directed to shampoo compositions comprising: (a) an effective amount of an optical brightener; (b) a 20 detergents surfactant suitable for cleansing the hair; and (c) a silicone compound.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

### DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed that the present invention will be better understood from the following description.

All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

#### OPTICAL BRIGHTENERS

Optical brighteners are compounds which absorb ultraviolet light and reemit the energy in the form of visible light. Specifically, the optical brighteners useful herein have an absorption, preferably a major absorption peak, between a wavelength of about 1nm and about 420nm, and an emission, preferably a major emission peak, between a wavelength of about 360nm and about 830nm; wherein the major absorption peak has a shorter wavelength than the major emission peak. More preferably, the optical brighteners useful herein have a major absorption peak between a wavelength of about 200nm and about 420nm, and a major emission peak between a wavelength of about 400nm and about 780nm. Optical brighteners may or may not have minor absorption peaks in the visible range between a wavelength of about 360nm and about 830nm. Optical brighteners can be described by other names in the art and in other industries, such as fluorescent whitening agents, fluorescent brighteners, and fluorescent dyes.

When applied to hair via suitable vehicles, optical brighteners herein provide benefits to the hair in three areas. First, optical brighteners herein alter the color of the hair by emitting light in the visible range. Second, optical brighteners herein enhance the shine of the hair by emitting light in the visible range. Third, optical brighteners herein protect the hair from ultraviolet light by absorbing ultraviolet light.

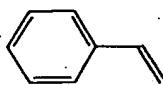
Optical brighteners in general are based on the structures of aromatic and heteroaromatic systems which provide these unique characteristics. The optical brighteners useful in the present invention can be classified according to their base structures, as described hereafter. Preferable optical brighteners herein include polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, and imidazoles.

Preferably, optical brighteners herein are included in the hair care composition of the present invention at a level by weight of from about 0.001% to about 20%, more preferably from about 0.01% to about 10%.

Polystyrylstilbenes

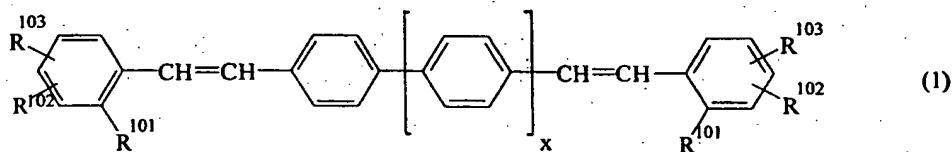
Polystyrylstilbenes are a class of compounds having two or more of the following base structure:

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Polystyrylstilbenes useful in the present invention include those having formulae (1), (2) and (3):



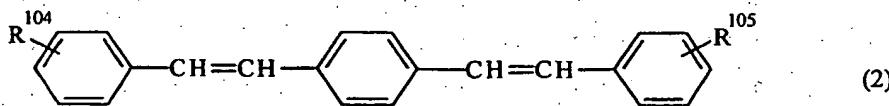
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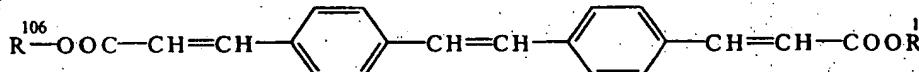
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wherein R<sup>101</sup> is H, OH, SO<sub>3</sub>M, COOM, OSO<sub>3</sub>M, OPO(OH)OM, wherein M is H, Na, K, Ca, Mg, ammonium, mono-, di-, tri- or tetra-C<sub>1</sub>-C<sub>30</sub>-alkylammonium, mono-, di- or tri-C<sub>1</sub>-C<sub>30</sub>-hydroxyalkylammonium or ammonium that is di- or tri-substituted with by a mixture of C<sub>1</sub>-C<sub>30</sub>-alkyl and C<sub>1</sub>-C<sub>30</sub>-hydroxyalkyl groups; or SO<sub>2</sub>N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, O-(C<sub>1</sub>-C<sub>30</sub>-alkyl), CN, Cl, COO(C<sub>1</sub>-C<sub>30</sub>-alkyl), CON(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub> or O(CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>X<sup>-</sup> wherein X<sup>-</sup> is an anion of a chloride, bromide, iodide, formate, acetate, propionate, glycolate, lactate, acrylate, methanephosphonate, phosphite, dimethyl or diethyl phosphite anion; CN, or alkyl of 1 to 30 carbons, R<sup>102</sup> and R<sup>103</sup>, independently, are H, SO<sub>3</sub>M wherein M is as previously defined; and x is 0 or 1; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably x is 1, R<sup>101</sup> is SO<sub>3</sub>Na and R<sup>102</sup> and R<sup>103</sup> are H; wherein the compound has a trans-coplanar orientation;



wherein R<sup>104</sup> and R<sup>105</sup>, independently, are CN, COO(C<sub>1</sub>-C<sub>30</sub>-alkyl), CONHC<sub>1</sub>-C<sub>4</sub>-alkyl, or CON(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>, wherein the compound has a trans-coplanar

orientation or cis-coplanar orientation; preferably R<sup>104</sup> and R<sup>105</sup> is 2-cyano, wherein the compound has a trans-coplanar orientation; and



(3)

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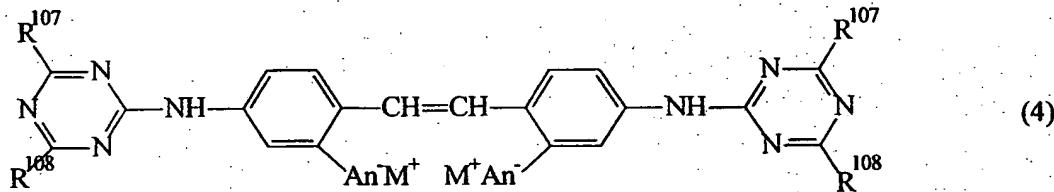
wherein each R<sup>106</sup>, independently, is H, or alkyl of 1 to 30 carbons; and wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

Suitable polystyrylstilbenes include disodium-1, 4'-bis(2-sulfostyryl) bisphenyl (C.I. Fluorescent Brightener 351) with tradename Tinopal CBS-X available from Ciba Specialty Chemicals, 1,4-bis(2-cyanostyryl)benzene (C.I. Fluorescent Brightener 199) with tradename Ultraphor RN available from BASF.

#### Triazinstilbenes

15 Triazinstilbenes are a class of compounds having both triazin and stilbene structures in the same molecule.

Triazinstilbenes useful in the present invention include those having formulae (4):



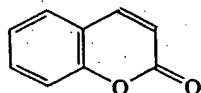
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wherein R<sup>107</sup> and R<sup>108</sup>, independently, are phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, N(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH), NH<sub>2</sub>, N(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>, OCH<sub>3</sub>, Cl, NH-(CH<sub>2</sub>)<sub>1-4</sub>SO<sub>3</sub>H or NH-(CH<sub>2</sub>)<sub>1-4</sub>OH; An<sup>-</sup> is an anion of a carboxylate, sulfate, sulfonate, or phosphate, and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>107</sup> is 2, 5-disulfophenylamino and each R<sup>108</sup> is morpholino; or each R<sup>107</sup> is 2, 5-disulfophenylamino and each R<sup>108</sup> is N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>; or each R<sup>107</sup> is 3-sulfophenyl and each R<sup>108</sup> is NH(CH<sub>2</sub>CH<sub>2</sub>OH) or N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>; or each R<sup>107</sup> is 4-sulfophenyl and each R<sup>108</sup> is N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>; and in each case, the sulfo group is SO<sub>3</sub>M in which M is sodium; wherein the compound has a trans-coplanar orientation.

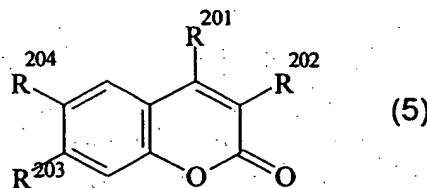
Suitable triazinstilbenes include 4,4'-bis-[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid with tradename Tinopal UNPA-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-morpholine-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal AMS-GX available from Ciba Specialty Chemicals, 4,4'-bis-[(4-anilino-6-(2-hydroxyethyl)methyl amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate with tradename Tinopal 5BM-GX available from Ciba Specialty Chemicals, 4'4'-bis-[(4,6-dianilino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-methylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, 4,4'-bis-[(4-anilino-6-ethylamino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disodium sulfonate, and 4,4'-bis(4-phenyl-1,2,3-triazol-2-yl)stilbene-2,2'-disulfonic acid.

#### Hydroxycoumarins

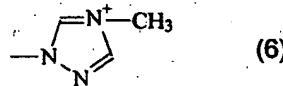
Hydroxycoumarins are a class of compounds having the following base coumarin structure and having at least one hydroxy moiety:



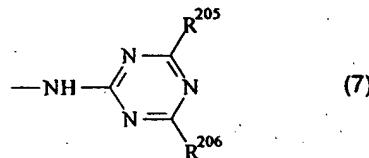
Hydroxycoumarins useful in the present invention include those having formulae (5):



wherein R<sup>201</sup> is H, OH, Cl, CH<sub>3</sub>, CH<sub>2</sub>COOH, CH<sub>2</sub>SO<sub>3</sub>H, CH<sub>2</sub>OSO<sub>3</sub>H, or CH<sub>2</sub>OPO(OH)OH, R<sup>202</sup> is H, phenyl, COO-C<sub>1</sub>-C<sub>30</sub>-alkyl, glucose, or a group of formula (6):



and R<sup>203</sup> is OH, or O-C<sub>1</sub>-C<sub>30</sub>-alkyl, and R<sup>204</sup> is OH or O-C<sub>1</sub>-C<sub>30</sub> alkyl, glycoside, or a group of the following formula (7):



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wherein R<sup>205</sup> and R<sup>206</sup> are independently, phenylamino, mono- or disulfonated phenylamino, morpholino, N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>2</sub>, N(CH<sub>3</sub>)(CH<sub>2</sub>CH<sub>2</sub>OH), NH<sub>2</sub>, N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, OCH<sub>3</sub>, Cl, NH-(CH<sub>2</sub>)<sub>1-4</sub>SO<sub>3</sub>H or NH-(CH<sub>2</sub>)<sub>1-4</sub>OH.

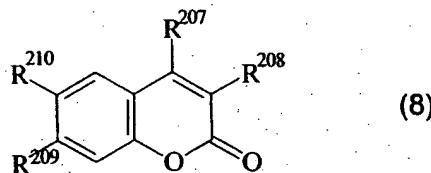
10 Suitable hydroxycoumarins include 6,7-dihydroxycoumarin available from Wako Chemicals, 4-methyl-7-hydroxycoumarin available from Wako Chemicals, 4-methyl-6,7-dihydroxycoumarin available from Wako Chemicals, esculin available from Wako Chemicals, and umbelliferone (4-hydroxycoumarin) available from Wako Chemicals.

#### Aminocoumarins

15 Aminocoumarins are a class of compounds having the base coumarin structure and having at least one amino moiety.

Aminocoumarins useful in the present inventions include those having formulae (8):

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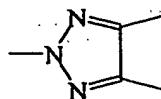


wherein R<sup>207</sup> is H, Cl, CH<sub>3</sub>, CH<sub>2</sub>COOH, CH<sub>2</sub>SO<sub>3</sub>H, CH<sub>2</sub>OSO<sub>3</sub>H, or CH<sub>2</sub>OPO(OH)OH, R<sup>208</sup> is H, phenyl, or COOC<sub>1</sub>-C<sub>30</sub> alkyl, and R<sup>209</sup> and R<sup>210</sup> are independently H, NH<sub>2</sub>, N(C<sub>1</sub>-C<sub>30</sub>alkyl)<sub>2</sub>, NHC<sub>1</sub>-C<sub>30</sub>alkyl, or NHCOC<sub>1</sub>-C<sub>30</sub>alkyl.

25 Suitable aminocoumarins include 4-methyl-7,7'-diethylamino coumarin with tradename Calcofluor-RWP available from BASF, 4-methyl-7,7'-dimethylamino coumarin with tradename Calcofluor-LD available from BASF.

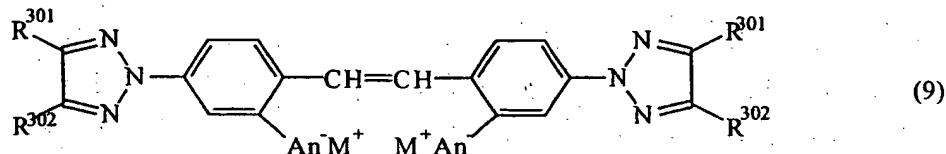
#### Triazoles

30 Triazoles are a class of compounds having the following base structure:



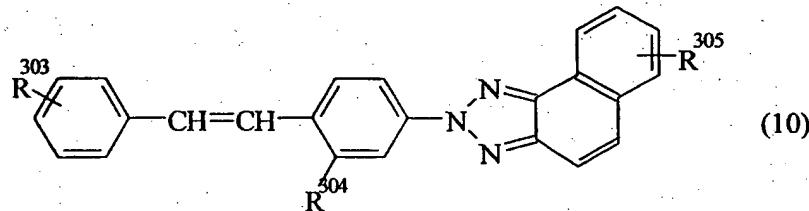
Triazoles useful in the present inventions include those having formulae (9) through (12) and (15) through (20):

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wherein R<sup>301</sup> and R<sup>302</sup>, independently, are H, C<sub>1</sub>-C<sub>30</sub>alkyl, phenyl or monosulfonated phenyl; An<sup>-</sup> and M are as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>301</sup> is phenyl, R<sup>302</sup> is H and M is sodium; wherein the compound has a trans-coplanar orientation;

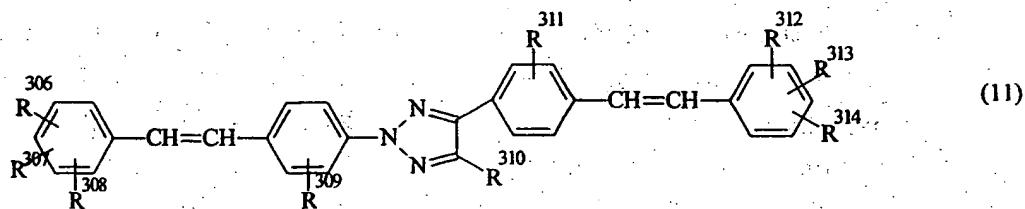
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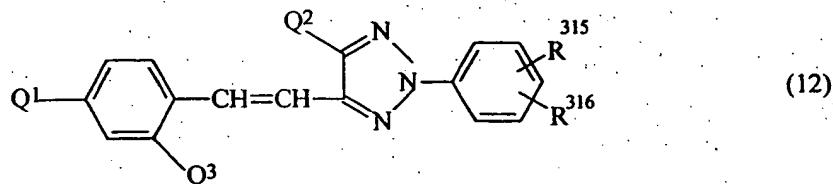
wherein R<sup>303</sup> is H or Cl; R<sup>304</sup> is SO<sub>3</sub>M, SO<sub>2</sub>N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, SO<sub>2</sub>O-phenyl or CN; R<sup>305</sup> is H, SO<sub>3</sub>M, COOM, OSO<sub>3</sub>M, or OPO(OH)OM; and M is as previously defined, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>303</sup> and R<sup>305</sup> are H and R<sup>304</sup> is SO<sub>3</sub>M in which M is Na; wherein the compound has a trans-coplanar orientation;

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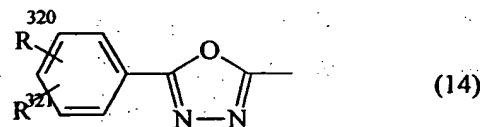
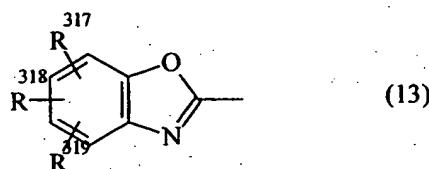
wherein each of R<sup>306</sup> and R<sup>312</sup> independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkylsulfonyl, arylsulfonyl, alkyl, alkoxy, aralkyl, aryl, aryloxy, aralkoxy or cycloalkyl radical, an unsubstituted or substituted 5-membered heterocyclic ring containing 2 to 3 nitrogen atoms or one oxygen atom and 1 or 2 nitrogen atoms, or together with R<sup>307</sup> and R<sup>313</sup> they represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R<sup>307</sup> and R<sup>313</sup> independently represents H, a sulfonic acid group or the salts, esters or amides thereof, a carboxylic acid group or the salts, esters or amides thereof, a cyano group, a halogen atom, an unsubstituted or substituted alkyl or alkoxy radical, or together with R<sup>306</sup> and R<sup>312</sup> represent a methylenedioxy, ethylenedioxy, methylenoxymethylenoxy, trimethylene, tetramethylene, propenylene, butenylene or butadienylene radical, each of R<sup>308</sup> and R<sup>314</sup> independently represents H, a halogen atom or an unsubstituted or substituted alkyl radical, each of R<sup>309</sup> and R<sup>311</sup> independently represents H, a halogen atom, a cyano group a sulonic acid group or the salts, esters or amides thereof, or a carboxylic acid group or the salts, esters or amides thereof, and R<sup>310</sup> independently represents H, a halogen atom, a cyano group a sulfonic acid group or the salts, alkyl radicals preferably by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, sulfonic acid groups, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; alkoxy radicals can be substituted by hydroxy, alkoxy of 1 to 30 carbon atoms, cyano, halogen, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, phenyl or phenoxy; phenyl, phenylalkyl or phenoxy radicals can be substituted by halogen, cyano, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, sulfo, or alkyl or alkoxy each of 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; possible cycloalkyl radicals are preferably cyclohexyl and cyclopentyl radicals which can be substituted by alkyl of 1 to 30 carbon atoms; possible 5-membered heterocyclic rings are v-triazole, oxazole or 1, 3, 4- oxdiazole radicals which can contain as substituents alkyl radicals of 1 to 4 carbon atoms, halogen, phenyl, carboxy, carbalkoxy having 1 to 30 carbon atoms in the alkoxy moiety, cyano, benzyl, alkoxy of 1 to 30 carbon atoms, phenoxy or sulfo, whilst two adjacent substituents of the triazole and oxazole radicals together are able to

form a substituted or unsubstituted fused benzene nucleus; wherein the compound has a trans-coplanar orientation;



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wherein Q<sup>1</sup> denotes one of the ring systems (13) or (14);



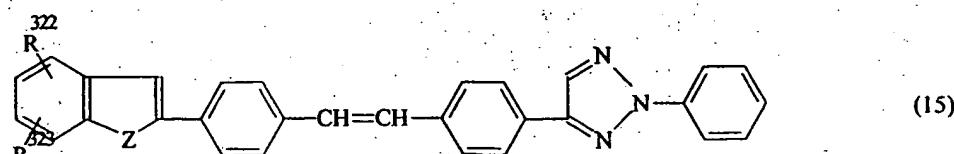
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and wherein R<sup>317</sup> denotes H, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with C<sub>1</sub>-C<sub>30</sub> carbon atoms in the alkyl part, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R<sup>318</sup>, denotes alkylene with 3 to 30 carbon atoms, R<sup>318</sup> denotes H or alkyl with 1 to 30 carbon atoms or, conjointly with R<sup>317</sup>, denotes alkylene with 3 to 30 carbon atoms, R<sup>319</sup> denotes H or methyl, R<sup>320</sup> denotes H, alkyl with 1 to 30 carbon atoms, phenyl, alkoxy with 1 to 30 carbon atoms, or Cl, or, conjointly with R<sup>321</sup>, denotes a fused benzene ring, R<sup>321</sup> denotes H or Cl or conjointly with R<sup>320</sup>, denotes a fused benzene ring, R<sup>315</sup> denotes H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms or Cl, R<sup>316</sup> denotes H or Cl, Q<sup>2</sup> denotes H, Cl alkyl with 1 to 30 carbon atoms or phenyl and Q<sup>3</sup> denotes H or Cl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;

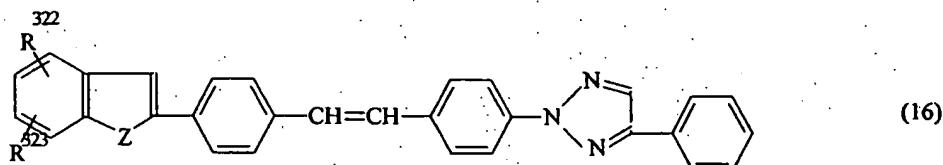
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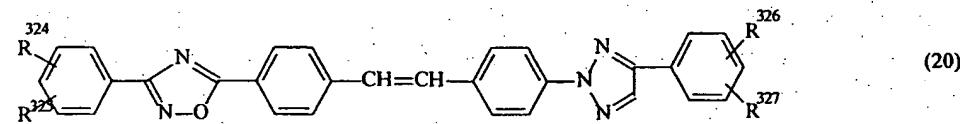
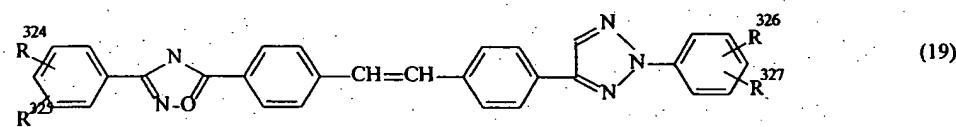
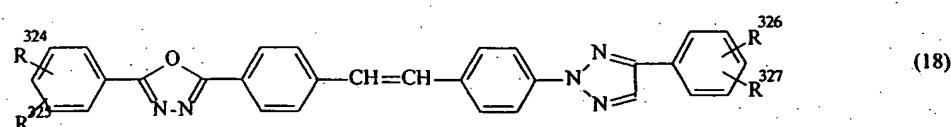
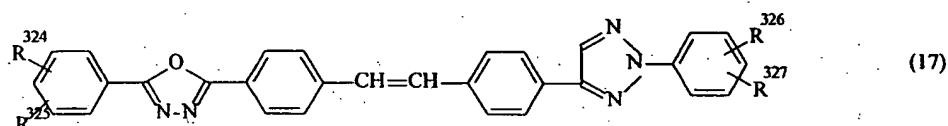
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25



wherein R<sup>322</sup> denotes H, Cl, methyl, phenyl, benzyl, cyclohexyl or methoxy,  
 R<sup>323</sup> denotes H or methyl and Z denotes O or S; wherein the compound has a  
 5 trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar  
 orientation; and



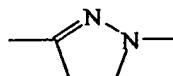
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wherein R<sup>324</sup> denotes H, Cl, alkyl with 1 to 30 carbon atoms, phenylalkyl with 1  
 15 to 30 carbon atoms, phenyl or alkoxy with 1 to 30 carbon atoms, or R<sup>324</sup>  
 conjointly with R<sup>325</sup> denotes a fused benzene radical, R<sup>325</sup> denotes H or methyl  
 or R<sup>325</sup> conjointly with R<sup>324</sup> denotes a fused benzene radical, R<sup>326</sup> denotes H,  
 alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy  
 with 1 to 30 carbon atoms or alkylsulfonyl with 1 to 30 carbon atoms and R<sup>327</sup>  
 denotes H, Cl, methyl or methoxy; wherein the compound has a trans-coplanar  
 20 orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

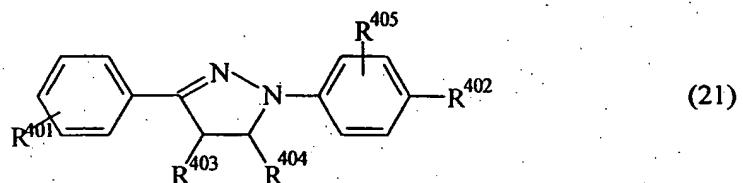
Suitable triazoles include 2-(4-styryl-3-sulfophenyl)-2H-naphtho[1,2-d]triazole (C.I. Fluorescent Brightener 46) with tradename Tinopal RBS available from Ciba Specialty Chemicals.

### Pyrazolines

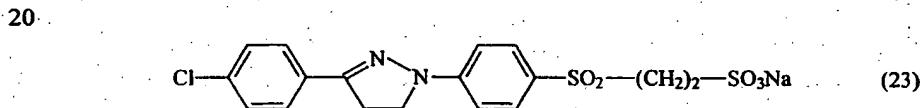
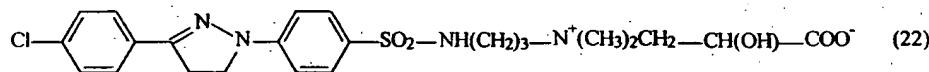
Pyrazolines are a class of compounds having the following base structure:



- 5 Pyrazolines useful in the present invention include those having formulae  
 (21) through (23):



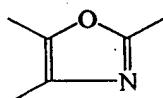
- 10 wherein R<sup>401</sup> is H, Cl or N(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>, R<sup>402</sup> is H, Cl, SO<sub>3</sub>M, SO<sub>2</sub>NH<sub>2</sub>,  
 SO<sub>2</sub>NH-(C<sub>1</sub>-C<sub>30</sub>alkyl), COO-C<sub>1</sub>-C<sub>30</sub>alkyl, SO<sub>2</sub>-C<sub>1</sub>-C<sub>30</sub>alkyl, SO<sub>2</sub>NH(CH<sub>2</sub>)<sub>1-4</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub> or SO<sub>2</sub>(CH<sub>2</sub>)<sub>1-4</sub>N<sup>+</sup>H(C<sub>1</sub>-C<sub>30</sub>-alkyl)<sub>2</sub>An<sup>-</sup>, R<sup>403</sup> and R<sup>404</sup> are the  
 same or different and each is H, C<sub>1</sub>-C<sub>30</sub>alkyl or phenyl and R<sup>405</sup> is H or Cl; and  
 An<sup>-</sup> and M are as previously defined, preferably R<sup>401</sup> is Cl, R<sup>402</sup> is SO<sub>2</sub>CH<sub>2</sub>  
 CH<sub>2</sub>N<sup>+</sup>H(C<sub>1</sub>-C<sub>4</sub>-alkyl)<sub>2</sub>An<sup>-</sup> in which An<sup>-</sup> is phosphite and R<sup>403</sup>, R<sup>404</sup> and R<sup>405</sup>  
 15 are each H; and formulae (22) and (23) shown below.



- Suitable pyrazolines include 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-  
 2-pyrazoline (C.I. Fluorescent Brightener 121) with trademark Blankophor DCB  
 25 available from Bayer, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(4-chlorophenyl)-2-  
 pyrazoline, 1-[4-(2-sulfoethylsulfonyl)phenyl]-3-(3,4-dichloro-6-methylphenyl)-2-  
 pyrazoline, 1-<4-{N-[3-(N,N,N-trimethylammonio)propyl]-amidosulfonyl}phenyl>-  
 3-(4-chlorophenyl)-2-pyrazoline methylsulfate, and 1-<4-{2-[1-methyl-2-(N,N-  
 dimethylamino)ethoxy]ethylsulfonyl}phenyl>-3-(4-chlorophenyl)-2-pyrazoline  
 30 methylsulfate.

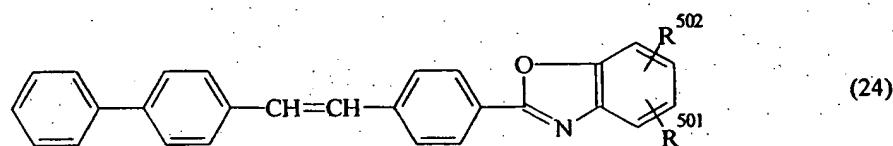
Oxazoles

Oxazoles are a class of compounds having the following base structure:



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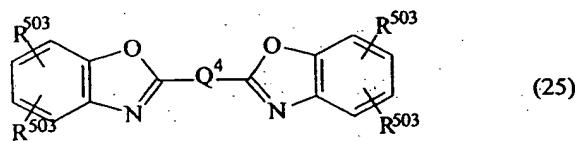
Oxazoles useful in the present inventions include those having formulae (24), (25), (26) and (27):



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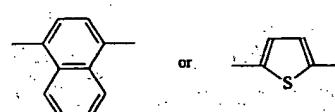
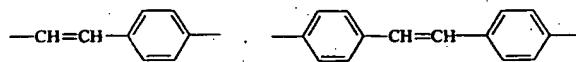
wherein R<sup>501</sup> and R<sup>502</sup>, independently, are H, Cl, C<sub>1</sub>-C<sub>30</sub>alkyl or SO<sub>2</sub>-C<sub>1</sub>-C<sub>30</sub>alkyl, wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>501</sup> is 4-CH<sub>3</sub> and R<sup>502</sup> is 2-CH<sub>3</sub> wherein the compound has a trans-coplanar orientation;

15



wherein R<sup>503</sup>, independently, is H, C(CH<sub>3</sub>)<sub>3</sub>, C(CH<sub>3</sub>)<sub>2</sub>-phenyl, C<sub>1</sub>-C<sub>30</sub>alkyl or COO-C<sub>1</sub>-C<sub>30</sub>alkyl, preferably H and Q<sup>4</sup> is -CH=CH-;

20



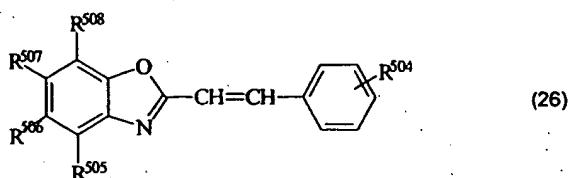
preferably



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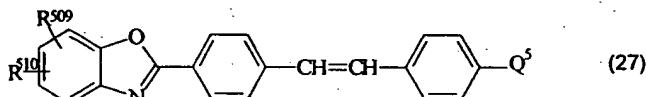
or one group R<sup>503</sup> in each ring is 2-methyl and the other R<sup>503</sup> is H and Q<sup>4</sup> is -CH=CH-; or one group R<sup>503</sup> in each ring is 2-C(CH<sub>3</sub>)<sub>3</sub> and the other R<sup>503</sup> is H; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation;

5



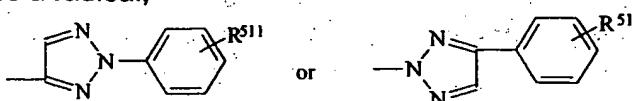
wherein R<sup>504</sup> is CN, Cl, COO-C<sub>1</sub>-C<sub>30</sub>alkyl or phenyl; R<sup>505</sup> and R<sup>506</sup> are the atoms required to form a fused benzene ring or R<sup>506</sup> and R<sup>508</sup>, independently, 10 are H or C<sub>1</sub>-C<sub>30</sub>alkyl; and R<sup>507</sup> is H, C<sub>1</sub>-C<sub>30</sub>alkyl or phenyl; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation; preferably R<sup>504</sup> is a 4-phenyl group and each of R<sup>505</sup> to R<sup>508</sup> is H; wherein the compound 15 has a trans-coplanar orientation; and

15



wherein R<sup>509</sup> denotes H, Cl, alkyl with 1 to 30 carbon atoms, cyclohexyl, phenylalkyl with 1 to 3 carbon atoms in the alkyl part, phenyl or alkoxy with 1 to 20

20 carbon atoms, R<sup>510</sup> denotes H or alkyl with 1 to 30 carbon atoms, and Q<sup>5</sup> denotes a radical;

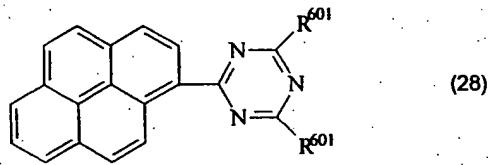


wherein R<sup>511</sup> represents H, alkyl with 1 to 30 carbon atoms, alkoxy with 1 to 30 carbon atoms, Cl, carbalkoxy with 1 to 30 carbon atoms, unsubstituted sulfamoyl or sulfamoyl which is monosubstituted or disubstituted by alkyl or hydroxyalkyl with 1 to 30 carbon atoms or represents alkylsulfonyl with 1 to 30 carbon atoms; wherein the compound has a trans-coplanar orientation or cis-coplanar orientation, preferably a trans-coplanar orientation.

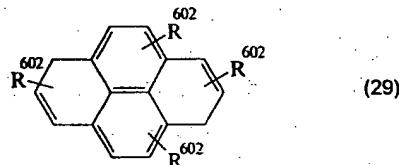
Suitable oxazoles include 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene, and 30 2-(4-methoxycarbonylstyryl)benzoxazole.

Pyrenes

Pyrenes useful in the present invention include those having formulae (28) and (29):



wherein each R601, independently, is C1-C30alkoxy; preferably methoxy; and



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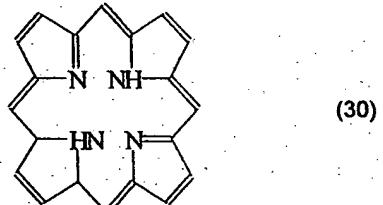
wherein each R602, independently, is H, OH, or SO<sub>3</sub>M, wherein M is as previously defined, sulfonated phenylamino, or anilino.

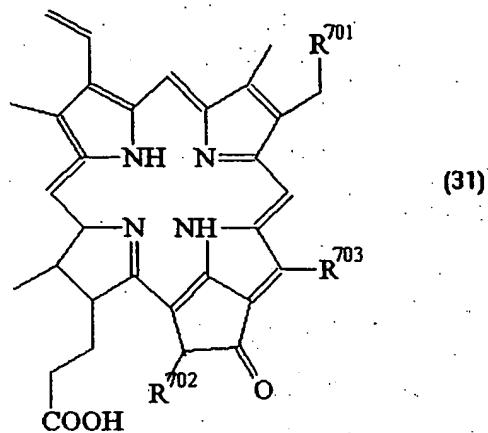
Suitable pyrenes include 2,4-dimethoxy-6-(1'-pyrenyl)-1,3,5-triazine (C.I. Fluorescent Brightener 179) with tradename Fluolite XMF, 8-hydroxy-1,3,6-pyrenetrisulfonic acid (D&C Green No.8), and 3-hydroxy-5,8,10-trisulphanilic pyrene.

Porphyrins

Porphyrins useful in the present invention include those having formulae (30), (31), and (32):

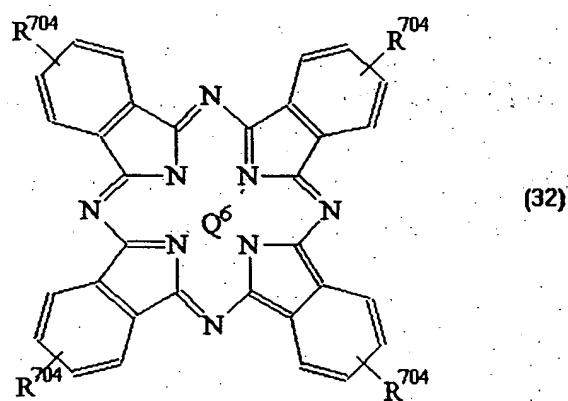
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wherein R701 is CH<sub>3</sub> or CHO, R702 is H or COOC<sub>1</sub>-C<sub>30</sub> alkyl, and R703 is H or an alkyl group having 1 to 30 carbons; and

5



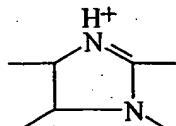
wherein each R704, independently, is H, SO<sub>3</sub>M, COOM, OSO<sub>3</sub>M, or OPO(OH)OM, wherein M is as previously defined, halide, or alkyl of 1 to 30 carbons; and Q6 is Cu, Mg, Fe, Cr, Co, or mixtures thereof with cationic charges.

Suitable porphyrins include porphyrin available from Wako Chemicals and Copper II phthalocyanine available from Wako Chemicals.

#### Imidazoles

Imidazoles are a class of compounds having the following base structure:

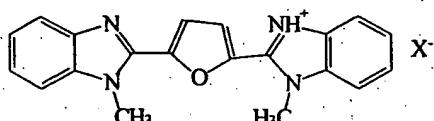
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Imidazoles useful in the present invention include those having formulae

(33):

5



(33)

wherein X- is as previously defined.

Suitable imidazoles include those with tradename of C.I. Fluorescence Brightener 352, or Uvtex AT available from Ciba Speciality Chemical.

### COMPOSITIONS

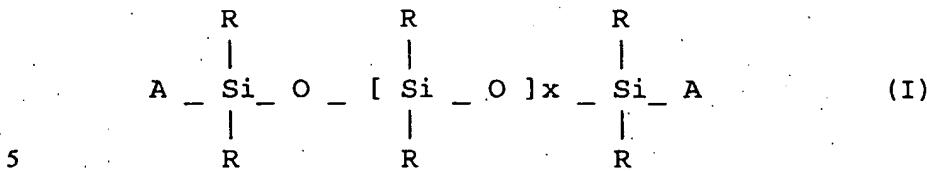
The hair care compositions of the present invention may comprise a component which characterizes the form of the product. Product forms useful herein include, but are not limited to, shampoo, conditioner, treatment, mousse, spray, lotion, gel, and cream products, all of which can be designed for rinse-off or leave-on convenience. Product functions useful herein include, but are not limited to, cleansing, and conditioning products. For example, a detergentsurfactant, a hair conditioning agent, and mixtures thereof may be comprised. The components and their levels are selected by one skilled in the art depending on the desired characteristic of the product.

### SILICONE COMPOUNDS

The hair care compositions of the present invention include a silicone compound, preferably at a level of from about 0.01% to about 15%. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone.

Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone compounds having hair conditioning properties can also be used.

The silicone compounds herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains 10 (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, 15 methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as 20 dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

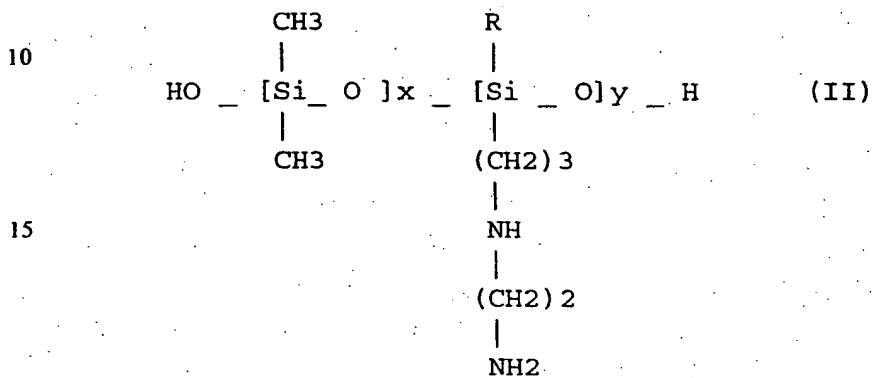
25 Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are 30 highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming 35 ability of the material.

The silicone compounds that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or

mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolymers.

5 Other silicone compounds include amino substituted materials. Suitable alkylamino substituted silicone compounds include those represented by the following structure (II)



10 15 20 wherein R is CH<sub>3</sub> or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

25 Suitable amino substituted silicone fluids include those represented by the formula (III)



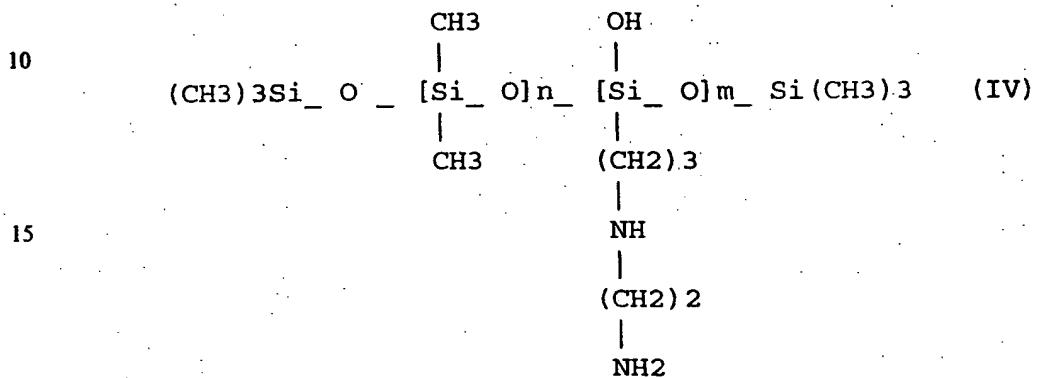
30 35 in which G is chosen from the group consisting of hydrogen, phenyl, OH, C<sub>1</sub>-C<sub>8</sub> alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R<sub>1</sub> is a monovalent radical of formula C<sub>q</sub>H<sub>2qL</sub> in which q is an integer from 2 to 8 and L is chosen from the groups

- N(R<sub>2</sub>)CH<sub>2</sub>-CH<sub>2</sub>-N(R<sub>2</sub>)<sub>2</sub>
- N(R<sub>2</sub>)<sub>2</sub>
- N(R<sub>2</sub>)<sub>3</sub>A-

-N(R<sub>2</sub>)CH<sub>2</sub>-CH<sub>2</sub>-NR<sub>2</sub>H<sub>2</sub>A-

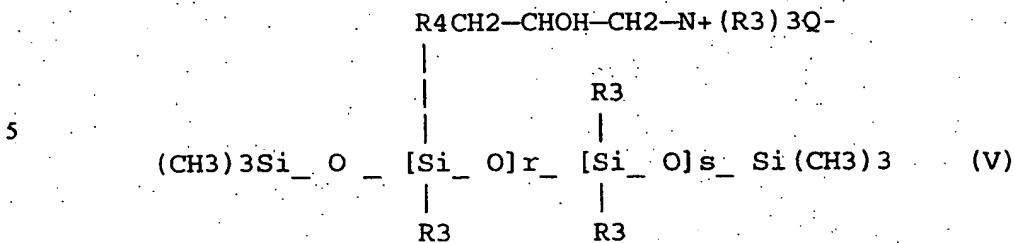
in which R<sub>2</sub> is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A- denotes a halide ion.

5 An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



20 In this formula n and m are selected depending on the exact molecular weight of the compound desired

Other amino substituted silicone polymers which can be used are represented by the formula (V):



10 where R3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R4 denotes a hydrocarbon radical, preferably a C1 - C18 alkylene radical or a C1 - C18, and more preferably C1 - C8, alkyleneoxy radical; Q- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 15 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone compounds include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This reference provides an extensive, though not exclusive, listing of suitable silicone compounds.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about

1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as Tospear<sup>TM</sup> from Toshiba Silicones.

The method of manufacturing these silicone compounds, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit  $(CH_3)_3SiO$ .5; D denotes the difunctional unit  $(CH_3)_2SiO$ ; T denotes the trifunctional unit  $(CH_3)SiO1.5$ ; and Q denotes the quadri- or tetra-functional unit  $SiO_2$ . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc.

The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system.

Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

#### DETERSIVE SURFACTANT

Compositions herein may include a detergents surfactant. The detergents surfactants herein are those suitable for cleansing the hair. Detergents surfactants useful herein include anionic surfactants, amphoteric and zwitterionic surfactants, and nonionic surfactants.

The detergents surfactants, when present, are preferably included at a level of from about 0.01% to about 75% by weight of the composition. Two or more surfactants can be used.

#### Anionic Surfactant

Anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials have the respective formulae  $ROSO_3M$  and  $RO(C_2H_4O)_xSO_3M$ , wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as

ammonium, alkanolammonium (e.g., triethanolammonium), a monovalent metal cation (e.g., sodium and potassium), or a polyvalent metal cation (e.g., magnesium and calcium). Preferably, M should be chosen such that the anionic surfactant component is water soluble. The anionic surfactant or surfactants 5 should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the anionic surfactant be soluble in the composition hereof.

Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration, 10 and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, 15 New York, USA), 1988 (ISBN 0-89573-399-0), which is incorporated by reference herein in its entirety.

In the alkyl and alkyl ether sulfates described above, preferably R has from about 8 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene 20 oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm oil, tallow, or the like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are reacted with 1 to about 10, and especially about 3, molar proportions of ethylene 25 oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

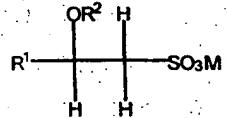
Specific examples of alkyl ether sulfates which can be used are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl 30 triethylene glycol ether sulfate; and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 8 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% 35 by weight C<sub>12-13</sub> compounds; from about 60% to about 100% by weight of C<sub>14-15-16</sub> compounds; from 0% to about 20% by weight of C<sub>17-18-19</sub>

compounds; from about 3% to about 30% by weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

Other suitable anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula [R<sup>1</sup>-SO<sub>3</sub>-M] where R<sup>1</sup> is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 8 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 8 to about 18 carbon atoms and a sulfonating agent, e.g., SO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C<sub>8</sub>-18 n-paraffins.

Still other suitable anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278, which are incorporated by reference herein in their entirety.

Another class of anionic surfactants suitable for use in the shampoo compositions are the β-alkyloxy alkane sulfonates. These compounds have the following formula:



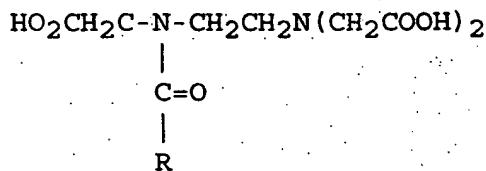
where R<sup>1</sup> is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R<sup>2</sup> is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C.

Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference in their entirety. Preferred anionic surfactants for use in the shampoo compositions include ammonium lauryl sulfate, ammonium laureth sulfate, triethylamine lauryl sulfate, triethylamine laureth sulfate, triethanolamine lauryl sulfate, triethanolamine laureth sulfate, monoethanolamine lauryl sulfate, monoethanolamine laureth sulfate, diethanolamine lauryl sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium lauryl sulfate, sodium laureth sulfate, potassium lauryl sulfate, potassium laureth sulfate, ammonium cocoyl sulfate, ammonium lauroyl sulfate, sodium cocoyl sulfate, sodium lauroyl sulfate, potassium cocoyl sulfate, potassium lauryl sulfate, triethanolamine lauryl sulfate, triethanolamine lauryl sulfate, monoethanolamine cocoyl sulfate, monoethanolamine lauryl sulfate, sodium tridecyl benzene sulfonate, and sodium dodecyl benzene sulfonate; and mixtures thereof.

Other anionic surfactants for use herein include polyhydrophilic anionic surfactants. By "polyhydrophilic" herein, is meant a surfactant that has at least two hydrophilic groups which provide a hydrophilic nature. Polyhydrophilic surfactants useful herein are only those having at least two hydrophilic groups in the molecule, and is not intended to encompass those which only have one hydrophilic group. One molecule of the polyhydrophilic anionic surfactant herein may comprise the same hydrophilic groups, or different hydrophilic groups. Specifically, the polyhydrophilic anionic surfactants comprise at least one group selected from the group consisting of carboxy, hydroxy, sulfate, sulfonate, and phosphate. Suitable polyhydrophilic anionic surfactants are those which comprise at least one of a carboxy, sulfate, or sulfonate group, more preferably those which comprise at least one carboxy group.

Nonlimiting examples of polyhydrophilic anionic surfactants include N-acyl-L-glutamates such as N-cocoyl-L-glutamate and, N-lauroyl-L-glutamate, laurimino dipropionate, N-acyl-L-aspartate, di-(N-lauroyl N-methyl taurate), polyoxyethylene laurylsulfosuccinate, disodium N-octadecylsulfosuccinate; disodium lauryl sulfosuccinate; diammonium lauryl sulfosuccinate; tetra sodium N-(1,2-dicarboxyethyl)-N-octadecylsulfosuccinate; the diamyl ester of sodium sulfosuccinic acid; the dihexyl ester of sodium sulfosuccinic acid; and the dioctyl ester of sodium sulfosuccinic acid, and 2-cocoalkyl N-carboxyethyl N-carboxyethoxyethyl imidazolinium betaine, lauroamphohydroxypropylsulfonate,

cocoglyceryl ether salts, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and those of the following formula:



wherein R is an alkyl of 8 to 18 carbons. Other polyhydrophilic anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO<sub>2</sub>, chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO<sub>2</sub>, etc., when used in the gaseous form. The α-olefins from which the olefin sulfonates are derived are mono-olefins having about 8 to about 24 carbon atoms, preferably about 10 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A specific α-olefin sulfonate mixture of the above type is described more fully in U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967, which is incorporated by reference herein in its entirety.

Another class of polyhydrophilic anionic surfactants are amino acid surfactants which are surfactants that have the basic chemical structure of an amino acid compound, i.e., that contains a structural component of one of the naturally-occurring amino acids. It is understood by the artisan that some surfactants may be regarded as both a polyhydrophilic anionic surfactant, and an amino acid surfactant. These surfactants are suitable anionic surfactants.

Nonlimiting examples of amino acid surfactants include, N-cocoylalaninate, N-acyl-N-methyl-β-alanate, N-acylsarcosinate; N-alkylamino propionates and N-alkyliminodipropionates, specific examples of which include

N-lauryl- $\beta$ -amino propionic acid or salts thereof, and N-lauryl- $\beta$ -imino-dipropionate, N-acyl-DL-alaninate, sodium lauryl sarcosinate, sodium lauroyl sarcosinate, lauryl sarcosine, cocoyl sarcosine, N-acyl-N-methyl taurate, lauroyl taurate, and lauroyl lactylate.

Commercially available anionic surfactants suitable are N-acyl-L-glutamate with a tradename AMISOFT CT-12S, N-acyl potassiumglycine with a tradename AMILITE GCK-12, lauroyl glutamate with a tradename AMISOFT LS-11, and N-acyl-DL-alaninate with tradename AMILITE ACT12 supplied by Ajinomoto; acylaspartate with tradenames ASPARACK and AAS supplied by Mitsubishi Chemical; and acyl derivatives of tradename ED3A supplied by Hampshire Chemical Corp.

Optionally the counter ion of anionic surfactants may be polyvalent cations. It has been found that these anionic surfactants, along with the cationic conditioning agents, and polyvalent metal cations as described later, form a coacervate in the compositions. Cationic conditioning agents may be included in the present composition to provide a shampoo which both cleanse and condition the hair from a single product.

Coacervate formulation is dependent upon a variety of criteria such as molecular weight, component concentration, and ratio of interacting ionic components ionic strength, charge density of the cationic and anionic components, pH, and temperature. Coacervate systems and the effect of these parameters are known in the art.

It is believed to be particularly advantageous, for the anionic surfactants and the polyvalent metal cations at certain levels to be present with the cationic conditioning agents in a coacervate phase. The coacervates formed in the compositions are believed to readily deposit on the hair upon diluting the coacervate with abundant water, i.e., rinsing of the shampoo.

Without being bound by theory, it is believed that the coacervates provide two major effects to the present shampoo composition. First, it reduces the Critical Micelle Concentration (hereinafter "CMC") of the composition. The reduction of the CMC relates to reduction of the surface tension, thereby improving lather performance. Second, the existence of the anionic surfactants along with the polyvalent metal cations expand the coacervate region in the composition. As the cationic conditioning agents in the composition are mainly delivered to the hair via these coacervates, expansion of the coacervate region results in delivery of more cationic conditioning agents to the hair. Consequently,

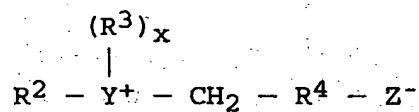
compositions which both cleanse and condition the hair from a single product, which have improved overall conditioning benefits and improved lathering are provided.

Techniques of analysis of formation of complex coacervates are known in the art. For example, microscopic analysis of the shampoo compositions, at any chosen stage of dilution, can be utilized to identify whether a coacervate phase has formed. Such coacervate phase will be identifiable as an additional emulsified phase in the composition. The use of dyes can aid in distinguishing the coacervate phase from other insoluble phases dispersed in the shampoo composition.

#### Amphoteric And Zwitterionic Surfactant

Amphoteric surfactants for use herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Zwitterionic surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:



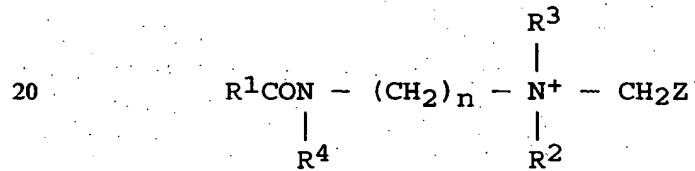
where  $\text{R}^2$  contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms;  $\text{R}^3$  is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom;  $\text{R}^4$  is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of amphoteric and zwitterionic surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example,

cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearyl amidododimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are 5 amidohydroxysultaines such as the C<sub>8</sub>-C<sub>18</sub> hydrocarbylamidopropyl hydroxysultaines, especially C<sub>8</sub>-C<sub>14</sub> hydrocarbylamidopropylhydroxysultaines, e.g., laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

10 Other suitable amphoteric surfactants are the aminoalkanoates of the formula RNH(CH<sub>2</sub>)<sub>n</sub>COOM, the iminodialkanoates of the formula RN[(CH<sub>2</sub>)<sub>m</sub>COOM]<sub>2</sub> and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

15 Other suitable amphoteric surfactants include those represented by the formula:

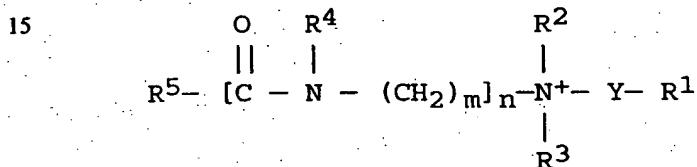


20 wherein R<sup>1</sup> is C<sub>8</sub> - C<sub>22</sub> alkyl or alkenyl, preferably C<sub>8</sub> - C<sub>16</sub>, R<sup>2</sup> and R<sup>3</sup> is independently selected from the group consisting of hydrogen, -CH<sub>2</sub>CO<sub>2</sub>M, -CH<sub>2</sub>CH<sub>2</sub>OH, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, or -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>m</sub>H wherein m is an integer from 1 to about 25, and R<sup>4</sup> is hydrogen, -CH<sub>2</sub>CH<sub>2</sub>OH, or CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOM, Z is CO<sub>2</sub>M or CH<sub>2</sub>CO<sub>2</sub>M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline intermediate. Suitable materials of this type are marketed under the tradename 30 MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R<sup>2</sup>. All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants, i.e. zwitterionic surfactants, suitable for use in the conditioning compositions are those represented by the formula:



wherein: R<sup>1</sup> is a member selected from the group consisting of COOM and CH(OH)CH<sub>2</sub>SO<sub>3</sub>M. R<sup>2</sup> is lower alkyl or hydroxyalkyl; R<sup>3</sup> is lower alkyl or hydroxyalkyl; R<sup>4</sup> is a member selected from the group consisting of hydrogen and lower alkyl; R<sup>5</sup> is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl, propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such

as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl- $\alpha$ -carboxyethylbetaine, cetyltrimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) carboxymethylbetaine, oleyldimethyl- $\gamma$ -carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)- $\alpha$ -carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyltrimethylsulfopropyl betaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful in the conditioning compositions include the amidocarboxybetaines, such as cocamido dimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, 15 cetylaminodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl) carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethyl sulfopropylbetaine, stearylaminodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

#### 20 Nonionic Surfactant

The compositions of the present invention can comprise a nonionic surfactant. Nonionic surfactants include those compounds produced by condensation of alkylene oxide groups, hydrophilic in nature, with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature.

Preferred nonlimiting examples of nonionic surfactants for use in the shampoo compositions include the following:

- (1) polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 20 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to from about 10 to about 60 moles of ethylene oxide per mole of alkyl phenol;
- (2) those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine products;
- (3) condensation products of aliphatic alcohols having from about 8 to about 18 carbon atoms, in either straight chain or branched chain configurations,

with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from about 10 to about 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from about 8 to about 14 carbon atoms;

(4) long chain tertiary amine oxides of the formula [ R<sup>1</sup>R<sup>2</sup>R<sup>3</sup>N → O ] where R<sup>1</sup> contains an alkyl, alkenyl or monohydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and R<sup>2</sup> and R<sup>3</sup> contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals;

(5) long chain tertiary phosphine oxides of the formula [RR'R"P → O] where R contains an alkyl, alkenyl or monohydroxyalkyl radical ranging from about 8 to about 18 carbon atoms in chain length, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties and R' and R" are each alkyl or monohydroxyalkyl groups containing from about 1 to about 3 carbon atoms;

(6) long chain dialkyl sulfoxides containing one short chain alkyl or hydroxy alkyl radical of from 1 to about 3 carbon atoms (usually methyl) and one long hydrophobic chain which include alkyl, alkenyl, hydroxy alkyl, or keto alkyl radicals containing from about 8 to about 20 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moieties;

(7) alkyl polysaccharide (APS) surfactants (e.g. alkyl polyglycosides), examples of which are described in U.S. Patent 4,565,647, which is incorporated herein by reference in its entirety, and which discloses APS surfactants having a hydrophobic group with about 6 to about 30 carbon atoms and a polysaccharide (e.g., polyglycoside) as the hydrophilic group; optionally, there can be a polyalkylene-oxide group joining the hydrophobic and hydrophilic moieties; and the alkyl group (i.e., the hydrophobic moiety) can be saturated or unsaturated, branched or unbranched, and unsubstituted or substituted (e.g., with hydroxy or cyclic rings); a preferred material is alkyl polyglucoside which is commercially available from Henkel, ICI Americas, and Seppic; and

(8) polyoxyethylene alkyl ethers such as those of the formula RO(CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>H and polyethylene glycol (PEG) glyceryl fatty esters, such as those of the formula R(O)OCH<sub>2</sub>CH(OH)CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>OH, wherein n is from 1 to about 200, preferably from about 20 to about 100, and R is an alkyl having from about 8 to about 22 carbon atoms.

35 CARRIER

The hair care composition of the present invention may comprise a carrier. The level and species of the carrier are selected according to the compatibility with other components, and desired characteristic of the product. For example, a high percentage of volatile solvents of low boiling point and/or propellant are suitably used for product forms aimed to be left on the hair. On the other hand, water solutions of volatile and non-volatile solvents are suitably used for product forms aimed to be rinsed off the hair after washing or treating the hair with the product.

The carrier useful in the present invention include volatile solvents, non-volatile solvents, propellants, and mixtures thereof.

Volatile solvents useful herein include water, lower alkyl alcohols having from 1 to 3 carbons, and hydrocarbons having from about 5 to about 8 carbons. The preferred volatile solvents are water, ethanol, isopropanol, pentane, hexane, and heptane. The water useful herein include deionized water and water from natural sources containing mineral cations. Deionized water is preferred.

Non-volatile solvents useful herein include alkyl alcohols having more than 3 carbons, and polyhydric alcohols. The polyhydric alcohols useful herein include 1,2-propane diol or propylene glycol, 1,3-propane diol, hexylene glycol, glycerin, diethylene glycol, dipropylene glycol, 1,2-butylene glycol, and 1,4-butylene glycol.

Propellants may be used for mousse and hair spray product forms. Propellants, when used in the present invention, are selected depending on variables such as the remainder of components, the package, and whether the product is designed to be used standing or invert.

Propellants useful herein include fluorohydrocarbons such as difluoroethane 152a (supplied by DuPont), dimethylether, and hydrocarbons such as propane, isobutane, n-butane, mixtures of hydrocarbons such as LPG (liquefied petroleum gas), carbon dioxide, nitrous oxide, nitrogen, and compressed air.

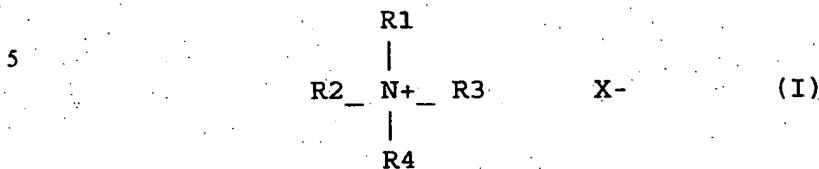
### CONDITIONING AGENTS

Conditioning agents useful herein include cationic surfactants, high melting point compounds, oily compounds, cationic polymers, and nonionic polymers. Conditioning agents may be present in the compositions herein either in combination with deteritive surfactant, or without deteritive surfactant.

#### Cationic Surfactant

The cationic surfactants useful herein are any known to the artisan.

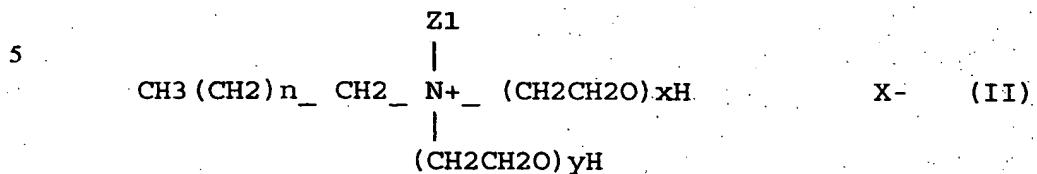
Among the cationic surfactants useful herein are those corresponding to the general formula (I):



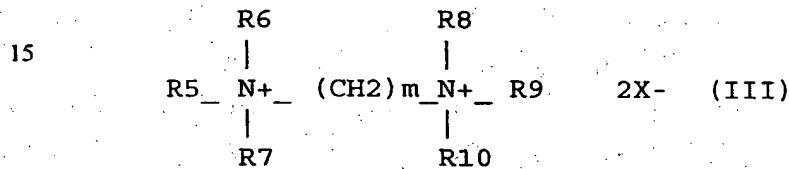
wherein at least one of R1, R2, R3, and R4 is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R1, R2, R3, and R4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R1, R2, R3, and R4 are independently selected from C1 to about C22 alkyl. Nonlimiting examples of cationic surfactants useful include the materials having the following CTFA designations: quaternium-8, quaternium-24, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-62, quaternium-70, quaternium-72, quaternium-75, quaternium-77, quaternium-78, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R1 - R4 radicals contain one or more hydrophilic moieties selected from alkoxy (preferably C1 - C3 alkoxy), polyoxyalkylene (preferably C1 - C3 polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically

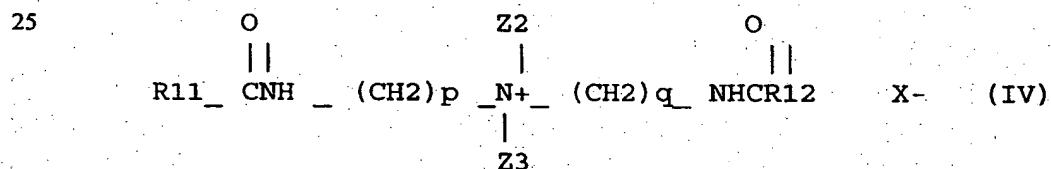
substituted cationic surfactants include those of the formula (II) through (VII) below:



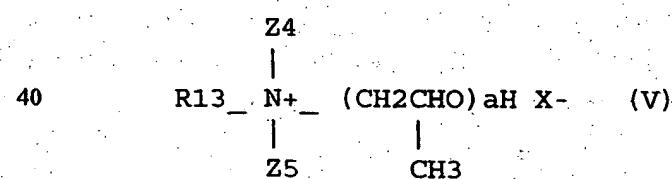
- 10 wherein n is from 8 to about 28, x+y is from 2 to about 40, Z1 is a short chain alkyl, preferably a C1 - C3 alkyl, more preferably methyl, or  $(\text{CH}_2\text{CH}_2\text{O})_z\text{H}$  wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



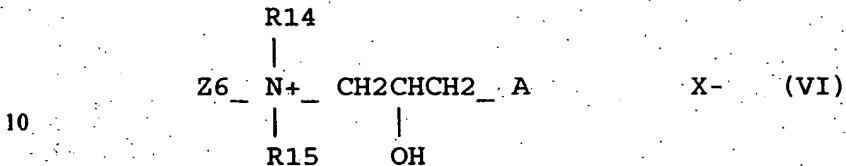
- 20 wherein m is 1 to 5, one or more of R5, R6, and R7 are independently an C1 - C30 alkyl, the remainder are  $\text{CH}_2\text{CH}_2\text{OH}$ , one or two of R8, R9, and R10 are independently an C1 - C30 alkyl, and remainder are  $\text{CH}_2\text{CH}_2\text{OH}$ , and X is a salt forming anion as mentioned above;



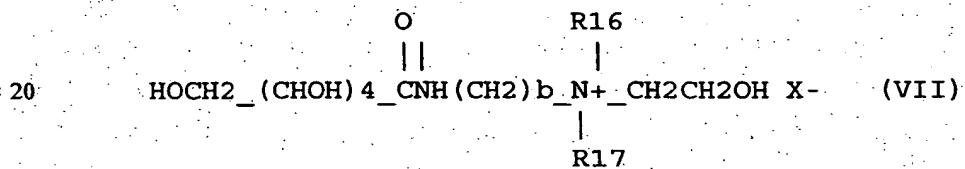
- 30 wherein Z2 is an alkyl, preferably a C1 - C3 alkyl, more preferably methyl, and Z3 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and q independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R11 and R12, independently, are substituted or unsubstituted hydrocarbyls, preferably C12 - C20 alkyl or alkenyl, and X is a salt forming anion as defined above;
- 35



wherein R13 is a hydrocarbyl, preferably a C1 - C3 alkyl, more preferably methyl, Z4 and Z5 are, independently, short chain hydrocarbyls, preferably C2 - C4 alkyl or alkenyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;



wherein R14 and R15, independently, are C1 - C3 alkyl, preferably methyl, Z6 is a C12 - C22 hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



wherein b is 2 or 3, R16 and R17, independently are C1 - C3 hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful include the materials having the following CTFA designations: quaternium-16, quaternium-61, quaternium-71, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein. Highly preferred compounds include commercially available materials of the following tradenames; VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about

12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amido substituted tertiary fatty amines. Such amines, useful herein, include stearamidopropyldimethylamine, stearamidopropydiethylamine, palmitamidopropyldimethylamine, palmitamidoethyldiethylamine, behenamidopropyldiethylamine, behenamidoethyldimethylamine, behenamidoethyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldimethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and 15 arachidylbehenylamine. These amines can also be used in combination with acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful are disclosed in U.S. 20 Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

High Melting Point Compound

The compositions may comprise a high melting point compound having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, 5 hydrocarbons, steroids, and mixtures thereof. Without being bound by theory, it is believed that these high melting point compounds cover the hair surface and reduce friction, thereby resulting in providing smooth feel on the hair and ease of combing. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one 10 classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, 15 certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, 20 both of which are incorporated by reference herein in their entirety.

The fatty alcohols useful herein are those having from about 14 to about 25 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein 35 include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds

having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; ceteareth 1 through ceteareth-10, which are the ethylene glycol ethers of ceteareth alcohol, i.e. a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C1-C30 alkyl ethers of the ceteth, steareth, and ceteareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate; polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20 carbons.

Steroids useful herein include compounds such as cholesterol.

High melting point compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By "pure" herein, what is meant is that the compound has a purity of at least about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having trademark 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA),

HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

Oily Compound

5 The compositions comprise an oily compound having a melting point of not more than about 25°C selected from the group consisting of a first oily compound, a second oily compound, and mixtures thereof. The oily compounds useful herein may be volatile or nonvolatile. Without being bound by theory, it is believed that, the oily compounds may penetrate the hair to modify the hydroxy bonds of the hair, thereby resulting in providing softness and flexibility to the hair. The oily compound may comprise either the first oily compound or the second oily compound as described herein. Preferably, a mixture of the first oily compound and the second oily compound is used. The oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992, both of which are incorporated by reference herein in their entirety.

First Oily Compound

20 The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, isostearyl alcohol, isocetyl alcohol, undecanol, octyl dodecanol, octyl decanol, octyl alcohol, caprylic alcohol, decyl alcohol and lauryl alcohol.

25 The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, isostearic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

30 The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and mixtures

thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, 5 octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, Oleth-2, pentaerythritol tetraoleate, pentaerythritol tetraisostearate, trimethylopropane trioleate, and trimethylopropane triisostearate.

Commercially available first oily compounds useful herein include: oleyl 10 alcohol with tradename UNJECOL 90BHR available from New Japan Chemical, pentaerythritol tetraisostearate and trimethylopropane triisostearate with tradenames KAKPTI and KAKTTI available from Kokyu Alcohol (Chiba, Japan), pentaerythritol tetraoleate having the same tradename as the compound name available from New Japan Chemical, trimethylopropane trioleate with a 15 tradename ENUJERUBU series available from New Japan Chemical, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol.

#### Second Oily Compound

20 The second oily compounds useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl 25 monomers, such as polymers of C2-6 alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain 30 lengths. The number average molecular weight of such materials can vary widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbon 35 materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane,

polybutene, polyisobutene, and mixtures thereof. Preferred for use herein are hydrocarbons selected from the group consisting of mineral oil, isododecane, isohexadecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available second oily compounds useful herein include  
5 isododecane, iso hexadecane, and isoeicosene with tradenames PERMETHYL  
99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse  
(South Plainfield New Jersey, USA), a copolymer of isobutene and normal  
butene with tradename INDOPOLE H-100 available from Amoco Chemicals  
(Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco,  
10 isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas,  
USA),  $\alpha$ -olefin oligomer with tradename PURESYN 6 from Mobil Chemical Co.,  
and trimethylolpropane tricaprylate/tricaprinate with tradename MOBIL ESTER P43  
from Mobil Chemical Co.

#### Cationic Polymers

15 As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

20 Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

25 The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

30 The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric

point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., 5 Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, 10 terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., 15 Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl 20 methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C1 - C7 alkyl groups, more preferably C1 - C3 alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

25 The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. 30 Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C1 - C7 alkyl, more preferably a C1 - C3 alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

35 Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate,

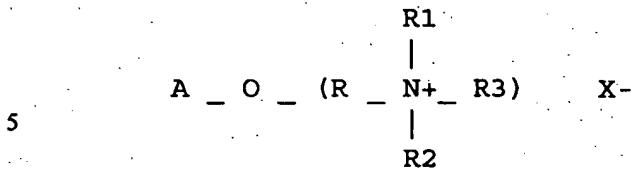
dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C1 - C3 alkyls, more preferably C1 and C2 alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C1 - C7 hydrocarbyls, more preferably C1 - C3 alkyls.

The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:



wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R1, R2, and R3 independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R1, R2 and R3) preferably being about 20 or less, and X is an anionic counterion, as previously described.

Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

#### Nonionic Polymer

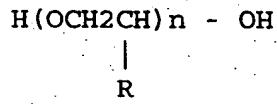
Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL, hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF

67, all supplied by Herculus. Other suitable nonionic polymers are ethylene oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

Polyalkylene Glycols

5 These compounds are particularly useful for compositions which are designed to impart a soft, moist feeling to the hair. When present, the polyalkylene glycol is typically used at a level from about 0.025% to about 1.5%, preferably from about 0.05% to about 1%, and more preferably from about 0.1% to about 0.5% of the compositions.

10 The polyalkylene glycols are characterized by the general formula:



15

wherein R is selected from the group consisting of H, methyl, and mixtures thereof. When R is H, these materials are polymers of ethylene oxide, which are also known as polyethylene oxides, polyoxyethylenes, and polyethylene glycols. When R is methyl, these materials are polymers of propylene oxide, which are also known as polypropylene oxides, polyoxypropylenes, and polypropylene glycols. When R is methyl, it is also understood that various positional isomers of the resulting polymers can exist.

In the above structure, n has an average value of from about 1500 to about 25,000, preferably from about 2500 to about 20,000, and more preferably from about 3500 to about 15,000.

20 Polyethylene glycol polymers useful herein are PEG-2M wherein R equals H and n has an average value of about 2,000 (PEG-2M is also known as Polyox WSR® N-10, which is available from Union Carbide and as PEG-2,000); PEG-5M wherein R equals H and n has an average value of about 5,000 (PEG-5M is also known as Polyox WSR® N-35 and Polyox WSR® N-80, both available from Union Carbide and as PEG-5,000 and Polyethylene Glycol 300,000); PEG-7M wherein R equals H and n has an average value of about 7,000 (PEG-7M is also known as Polyox WSR® N-750 available from Union Carbide); PEG-9M wherein R equals H and n has an average value of about 9,000 (PEG-9-M is also known as Polyox WSR® N-3333 available from Union Carbide); and PEG-14 M wherein R equals H and n has an average value of about 14,000 (PEG-14M is also known as Polyox WSR® N-3000 available from Union Carbide).

Other useful polymers include the polypropylene glycols and mixed polyethylene/polypropylene glycols.

#### ADDITIONAL COMPONENTS

The compositions of the present invention may include a variety of additional components, which may be selected by the artisan according to the desired characteristics of the final product. Additional components include, for example, polyvalent metal cations, suspending agents, and other additional components.

#### Polyvalent Metal Cations

Suitable polyvalent metal cations include divalent and trivalent metals, divalent metals being preferred. Exemplary metal cations include alkaline earth metals, such as magnesium, calcium, zinc, and copper, and trivalent metals such as aluminum and iron. Preferred are calcium and magnesium.

The polyvalent metal cation can be added as an inorganic salt, organic salt, or as a hydroxide. The polyvalent metal cation may also be added as a salt with anionic surfactant, including the primary anionic surfactants as mentioned above, or detergents as mentioned below.

Preferably, the polyvalent metal cation is introduced as an inorganic salt or organic salt. Inorganic salts include chloride, bromide, iodine, nitrate, or sulfate, more preferably chloride or sulfate. Organic salts include L-glutamate, lactate, malate, succinate, acetate, fumarate, L-glutamic acid hydrochloride, and tartarate.

It will be clear to those skilled in the art that, if polyvalent salts of the anionic surfactant is used as the mode of introducing the polyvalent metal cations into the compositions hereof, only a fraction of the anionic surfactant may be of polyvalent form, the remainder of the anionic surfactant being necessarily added in monovalent form.

Hardness of the conditioning shampoo compositions can be measured by standard methods in the art, such as by ethylene diamine tetraacetic acid (EDTA) titration. In the event that the composition contains dyes or other color materials that interfere with the ability of EDTA titration to yield a perceptible color change, hardness should be determined from the composition in the absence of the interfering dye or color.

#### Suspending Agents

A preferred additional component is a suspending agent, particularly for compositions comprising silicone compounds of high viscosity and/or large

particle size. When present, the suspending agent is in dispersed form in the compositions. The suspending agent will generally comprise from about 0.1% to about 10%, and more typically from about 0.3% to about 5.0%, by weight, of the composition.

Preferred suspending agents include acyl derivatives such as ethylene glycol stearates, both mono and distearate, long chain amine oxides such as alkyl (C16-C22) dimethyl amine oxides, e.g., stearyl dimethyl amine oxide, and mixtures thereof. When used in the shampoo compositions, these preferred suspending agents are present in the composition in crystalline form. These suspending agents are described in U.S. Patent 4,741,855.

Other suitable suspending agents include alkanol amides of fatty acids, preferably having from about 16 to about 22 carbon atoms, more preferably about 16 to 18 carbon atoms, preferred examples of which include stearic monoethanolamide, cocomonoethanolamide, stearic diethanolamide, stearic monoisopropanolamide and stearic monoethanolamide stearate.

Other suitable suspending agents include N,N-dihydrocarbyl amido benzoic acid and soluble salts thereof (e.g., Na and K salts), particularly N,N-di(hydrogenated) C16, C18 and tallow amido benzoic acid species of this family, which are commercially available from Stepan Company (Northfield, Illinois, USA).

Other suitable suspending agents include xanthan gum. The use of xanthan gum as a suspending agent in silicone containing shampoo compositions is described, for example, in U.S. Patent 4,788,006, which is incorporated herein by reference in its entirety. Combinations of long chain acyl derivatives and xanthan gum may also be used as a suspending agent in the shampoo compositions. Such combinations are described in U.S. Patent 4,704,272, which is incorporated herein by reference in its entirety.

Other suitable suspending agents include carboxyvinyl polymers. Preferred among these polymers are the copolymers of acrylic acid crosslinked with polyallylsucrose as described in U.S. Patent 2,798,053, which is incorporated herein by reference in its entirety. Examples of these polymers include the carbomers, which are homopolymers of acrylic acid crosslinked with an allyl ether of pentaerythritol, an allyl ether of sucrose, or an allyl ether of propylene. Neutralizers may be required, for example, amino methyl propanol, triethanol amine, or sodium hydroxide.

Other suitable suspending agents can be used in the compositions, including those that can impart a gel-like viscosity to the composition, such as water soluble or colloidally water soluble polymers like cellulose ethers such as hydroxyethyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, and materials such as guar gum, polyvinyl alcohol, polyvinyl pyrrolidone, hydroxypropyl guar gum, starch and starch derivatives.

Other Additional Components

A wide variety of other additional ingredients can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Peptein 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, and antidandruff agents such zinc pyridinethione. Such optional ingredients generally are used individually at levels from about 0.001% to about 10.0%, preferably from about 0.01% to about 5.0% by weight of the composition.

**EXAMPLES**

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

Method of Preparation

The hair spray, mousses, lotions and conditioners are suitably made as follows: If included in the formula, polymeric materials are dispersed in water at room temperature. If required, the polymeric materials such as Carbomer and Acrylates/Stearth-20 Methacrylate Copolymer may be neutralized after dispersing. The mixture is then heated up to above 60°C, and fatty alcohols and emulsifiers are added if included in the formulation. After cooling down to below 50°C, the remaining components are added with agitation then cooled down to about 30°C. Ethanol is added here if included in the formula. A triblender and mill can be used if necessary to disperse the materials. As appropriate, the mixture thus obtained can be packed into an aerosol can with propellant.

The shampoos are suitably prepared by any conventional method well known in the art. A suitable method is as follows: polymer and surfactants are dispersed in water to form a homogenous mixture. To this mixture are added the other ingredients except for silicone emulsion (if present), perfume, and salt; the obtained mixture is agitated. If present, the silicone emulsion is made with Dimethicone or Dimethiconol, a small amount of deterutive surfactant, and a portion of water. The obtained mixture is then passed through a heat exchanger to cool, and the silicone emulsion, perfume, and salt are added. The obtained compositions are poured into bottles to make hair shampoo compositions.

Alternatively, water and surfactants and any other solids that need to be melted can be mixed together at elevated temperature, e.g., above about 70°C, to speed the mixing into shampoo. Additional ingredients can be added either to this hot premix or after cooling the premix. The ingredients are mixed thoroughly at the elevated temperature and then pumped through a high shear mill and then through a heat exchanger to cool them to ambient temperature. If present in the composition, silicone emulsified at room temperature in concentrated surfactant is added to the cooled mix.

Compositions

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	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Disodium-1,4-bis(2-sulfostyryl)biphenyl *1	1.0	-	-	-	-	-
4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl)-amino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acids *2	-	0.8	-	-	-	-

4-methyl-6,7-dihydroxycoumarin *3	-	-	1.0	-	-	-
4-methyl-7,7'-dimethylamino coumarin *4	-	-	-	0.1	-	-
2-(4-styryl-3-sulfophenyl)-2H-naphto[1,2-d]triazole	-	-	-	1.0	-	-
1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline *5	-	-	-	-	0.5	-
2,4-dimethoxy-6-(1'pyrenyl)-1,3,5-triazine *6	-	-	-	-	-	1.0
Silicone	3.0	2.0	2.0	3.0	1.6	2.0
Silicone Emulsion *15	-	-	-	-	-	-
Ammonium Laureth-3 Sulfate	12.0	12.0	12.0	15.0	10.0	10.0
Ammonium Lauryl Sulfate	2.0	2.0	2.0	2.0	-	-
N-acyl-L-gultamate Triethanolamine *9	2.0	2.0	-	-	2.0	2.0
Sodium Lauroyl Sarcosinate *10	-	-	2.0	2.0	2.0	1.0
Cocamidopropylbetaine *11	2.0	4.0	4.0	4.0	2.0	2.0
Laureth-20 *12	-	0.5	-	0.5	0.5	-
Alkyl polyglucoside *13	1.0	-	1.0	-	-	-
Ethylene Glycol Distearate *14	2.0	2.0	2.0	2.0	2.0	1.5
Cocamide MEA	1.5	1.5	1.5	1.5	1.5	1.5
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2	0.2
Magnesium chloride	0.5	-	0.5	-	-	-
Glycerin *7	-	-	5.0	-	-	-
Propylene Glycol *8	1.0	3.0	-	10.0	5.0	10.0
Polyoxyethylene Glycol *16	-	0.2	-	0.1	0.5	-
Hydroxyethyl Cellulose *17	0.1	-	0.1	-	-	0.5
Polyquaternium-10 *18	0.5	0.4	-	-	-	-
Monoalkyl trimethyl ammonium	-	-	0.1	-	-	-
Cetyl Alcohol *19	0.2	0.1	-	0.1	0.1	-
Stearyl Alcohol *20	-	-	-	0.1	0.2	-
Behenyl Alcohol *21	-	-	0.1	-	-	-
Perfume	0.5	0.5	0.5	0.5	0.5	0.5
Pentaerythritol Tetraisostearate *22	-	-	1.0	0.5	-	-
Trimethylolpropane Triisostearate *23	0.5	-	-	-	0.3	-
Pentaerythritol Tetraoleate	-	0.3	-	-	-	-

Trimethylolpropane Trioleate *24	-	-	-	-	-	0.5
Monosodium phosphate	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5
Disodium phosphate	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5
Hydrolyzed Collagen *40	0.01	-	-	-	-	-
Vitamin E *41	0.01	-	-	-	-	-
Panthenol *42	0.025	-	-	-	-	-
Panthenyl Ethyl Ether *43	0.225	-	-	-	-	-
Deionized Water	q.s. to 100%					

	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Disodium-1,4-bis(2-sulfostyryl) biphenyl *1	0.8	1.0	0.5	0.8
Silicone	2.0	-	-	-
Silicone Emulsion *15	-	2.0	2.0	1.0
Ammonium Laureth-3 Sulfate	12.0	12.0	15.0	10.0
Ammonium Lauryl Sulfate	2.0	2.0	2.0	2.0
Sodium Lauroyl Sarcosinate *10	-	-	-	1.0
Cocamidopropylbetaine *11	-	-	-	2.0
Cocamide MEA	1.5	1.5	1.5	1.5
DMDM Hydantoin	0.2	0.2	0.2	0.2
Monosodium phosphate	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5
Disodium phosphate	0 to 0.5	0 to 0.5	0 to 0.5	0 to 0.5
Deionized Water	q.s. to 100%			

	Ex.11	Ex.12	Ex.13	Ex.14	Ex.15
Disodium-1,4-bis(2-sulfostyryl)biphenyl *1	0.80	-	-	0.10	-
4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl)amino	-	-	-	-	0.80
1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acids *2					
1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline *5	-	-	-	0.60	-
4,4'-bis(5-methylbenzoxazol-2-yl)stilbene *25	-	-	0.50	-	-

2,4-dimethoxy-6-(1'pyrenyl)-1,3,5-triazine *6	-	0.20	-	-	-
Silicone Emulsion *15	1.00	0.50	2.00	0.20	1.00
Cetyl Alcohol *19	2.00	0.50	0.60	0.20	0.60
Stearyl Alcohol *20	3.00	0.50	0.40	0.20	0.40
Behenyl Alcohol *21	-	-	-	0.20	-
Polysorbate 60 *26	1.00	-	-	-	-
Lauryl Methyl Gluceth-10	-	1.00	-	0.50	-
Hydroxypropyl-dimonium Chloride *27					
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate *28	-	-	0.10	-	0.10
Citric Acid *29	0-0.2	0-0.2	0-0.2	0-0.2	-
Hydroxyl Propyl Cellulose *30	-	-	-	-	0.50
Polyoxyethylene Glycol *16	0.50	0.50	0.50	0.50	0.50
Aminomethylpropanol *31	2.10	-	2.10	-	-
Acrylates/Steareth-20 Methacrylate Copolymer *32	1.75	-	1.75	-	-
Cetyl Hydroxyethyl Cellulose *33	-	0.75	-	0.75	-
Polyquaternium-10 *18	0.10	-	0.10	0.20	-
Polyquaternium-7 *34	-	0.50	-	-	1.00
Pentaerythritol Tetraisostearate *22	1.00	3.00	-	-	-
Trimethylolpropane Trioleate *24	-	-	0.50	-	0.10
Trimethylolpropane Triisostearate *23	-	-	-	0.20	-
Preservatives	0.90	0.90	0.90	0.90	-
Perfume	0.08	0.08	0.08	0.08	0.08
Glycerin *7	-	-	5.00	-	-
Propylene Glycol *8	-	-	-	5.00	-
Denatured Ethyl Alcohol	-	-	-	-	18.98
Deionized Water	q.s. to 100%				

	Ex.16	Ex.17	Ex.18	Ex.19
4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl)amino1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acids *2	0.80	-	-	-
4-methyl-6,7-dihydroxycoumarin *3	-	0.50	-	-

4-methyl-7,7'-dimethylamino coumarin *4	-	-	0.50	-
2-(4-styryl-3-sulfophenyl)-2H-naphto[1,2-d]triazole	-	-	-	0.40
15/85 Silicone Blend *35	-	-	-	4.20
Silicone Emulsion *15	0.20	0.50	1.00	
Cetyl Alcohol *19	0.20	-	2.00	2.50
Stearyl Alcohol *20	0.20	-	-	4.50
Behenyl Alcohol *21	0.10	0.50	-	-
Stearamidopropyl dimethylamine *36	0.20	-	-	2.00
L-Glutamic Acid *37	0.08	-	-	0.64
Hydroxyethyl Cellulose *17	-	0.50	-	-
Polyoxyethylene Glycol *16	0.50	0.50	0.50	0.20
Carbomer *38	0.50	-	0.50	-
Aminomethylpropanol *31	0.60	-	0.60	-
Polyquaternium-10 *18	1.00	0.10	-	0.20
Polyquaternium-7 *34	-	-	0.50	-
Pentaerythritol Tetraisostearate *22	0.10	0.10	0.20	-
Trimethylolpropane Trioleate *24	0.10	0.10	0.05	-
Trimethylolpropane Triisostearate	-	-	-	0.25
Preservatives	-	-	-	0.53
Perfume	0.08	0.08	0.08	0.20
Glycerin *7	-	5.00	-	-
Propylene Glycol *8	-	-	5.00	-
Denatured Ethyl Alcohol	19.07	18.42	17.81	-
Deionized Water	q.s. to 100%			

	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex. 25
Disodium-1,4-bis(2-sulfostyryl)biphenyl *1	0.80	1.60	0.20	1.60	0.20	0.20
15/85 Silicone Blend *35	-	-	-	-	4.20	4.20
Silicone Emulsion *15	1.00	1.00	1.00	0.50	-	-
Cetyl Alcohol *19	-	-	-	-	2.50	2.50
Stearyl Alcohol *20	-	-	-	-	4.50	4.50
Alkyl Trimethyl Ammonium Chloride *39	-	-	-	-	-	2.50

Stearamidopropyl dimethylamine *36	-	-	-	-	2.00	-
L-Glutamic Acid *37	-	-	-	-	0.64	-
Preservatives	0.90	0.90	-	-	0.53	0.53
Perfume	0.08	0.08	0.08	0.08	0.20	0.20
Denatured Ethyl Alcohol	-	-	19.74	19.56	-	-
Deionized Water	-----q.s. to 100%-----					

Definitions

- \*1 Disodium-1,4-bis(2-sulfostyryl)biphenyl: TINOPAL CBX obtained by Ciba Geigy.
- 5 \*2 4,4'-bis[(4-anilino-6-bis(2-hydroxyethyl)amino-1,3,5-triazin-2-yl)amino] stilbene-2,2'-disulfonic acids: Tinopal UNPA-GX obtained by Ciba Geigy.
- \*3 4-methyl-6,7-dihydroxycoumarin: available from Wako.
- \*4 4-methyl-7,7'-dimethylamino coumarin: available from Wako.
- \*5 1-(4-amidosulfonylphenyl)-3-(4-chlorophenyl)-2-pyrazoline: Blankophor.
- 10 DCB obtained by Bayer.
- \*6 2,4-dimethoxy-6-(1'pyrenyl)-1,3,5-triazine: available from Ciba Geigy.
- \*7 Glycerin: Glycerin USP obtained by Nihon Yushi.
- \*8 Propylene Glycol: Lexol PG-865 obtained by Inolex.
- \*9 N-acyl-L-gultamate Triethanolamine: CT12S obtained by Ajinomoto.
- 15 \*10 Sodium Lauroyl Sarcosinate: Soypon obtained by Kawaken Fine Chem.
- \*11 Cocamidopropylbetaine: Tegobetain obtained by Th.Goldschmidt AG.
- \*12 Laureth-20: BL-20 obtained by Nikko.
- \*13 Alkyl polyglucoside: Plantacare 2000UP obtained by Henkel.
- \*14 Ethylene Glycol Distearate: EGDS obtained by Th. Goldschmidt AG.
- 20 \*15 Silicone Emulsion: X65-4829 obtained by Tosil/GE.
- \*16 Polyoxyethylene Glycol: WSR N-10 obtained by Amerchol.
- \*17 Hydroxyethyl Cellulose: available from Aqualon.
- \*18 Polyquaternium-10: UCARE Polymer LR 400 obtained by Amerchol.
- \*19 Cetyl Alcohol: Konol series obtained by Shinihon Rika.
- 25 \*20 Stearyl Alcohol: Konol series obtained by Shinihon Rika.
- \*21 Behenyl Alcohol: 1-Docosanol ( 97%) obtained by Wako.
- \*22 Pentaerythritol Tetraisostearate: KAK PTI obtained by Kokyu alcohol.
- \*23 Trimethylolpropane Triisostearate: KAK TTI obtained by Kokyu alcohol.

- \*24 Trimethylopropane Trioleate: Enujerubu TP3SO obtained by Shinohon Rika.
- \*25 4,4'-bis(5-methylbenzoxazol-2-yl)stilbene: available from TCI.
- \*26 Polysorbate 60: Tween 60 obtained by ICI.
- 5 \*27 Lauryl Methyl Gluceth-10 Hydroxypropylmonium Chloride: Glucquat 125 obtained by Amerchol.
- \*28 Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate: Varisoft 110 obtained by Witco.
- \*29 Citric Acid: Anhydrous Citric acid obtained by Haarman & Reimer.
- 10 \*30 Hydroxyl Propyl Cellulose: Metlose obtained by Shinetsu.
- \*31 Aminomethylpropanol: AMP-regular obtained by Angus.
- \*32 Acrylates/Steareth-20 Methacrylate Copolymer: Aculyn obtained by Rohm&Haas.
- \*33 Cetyl Hydroxyethyl Cellulose: Polysurf 67 obtained by Aqualon.
- 15 \*34 Polyquaternium-7: Merquat S obtained by Calgon.
- \*35 15/85 Silicone Blend: available from Shinetsu.
- \*36 Stearamidopropyl dimethylamine: Amidoamine MPS obtained by Nikko.
- \*37 L-Glutamic Acid: L-Glutamic acid (cosmetic grade) obtained by Ajinomoto.
- \*38 Carbomer: Carbopol 980 obtained by BF Goodrich.
- 20 \*39 Alkyl Trimethyl Ammonium Chloride: available from TOHO.
- \*40 Hydrolyzed Collagen: PEPTEIN 2000 obtained by Hormel.
- \*41 Vitamin E: EMIX-d obtained by Eisai.
- \*42 Panthenol: available from Roche.
- \*43 Panthenyl Ethyl Ether: available from Roche.

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The embodiments disclosed and represented by the previous examples have many advantages. For example, they can provide the benefits associated with optical brighteners (e.g., shine, UV protection, color alteration) while also providing desirable conditioning attributes such as good combing, shininess, and improved hair gloss and sheen.

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It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

**What is claimed is:**

1. A hair care composition comprising:
  - (a) an effective amount of an optical brightener selected from the group consisting of polystyrylstilbenes, hydroxycoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof; and
  - (b) a silicone compound.
2. The hair care composition of claim 1 further comprising a carrier suitable for application to the hair.
3. A hair care composition comprising:
  - (a) an effective amount of an optical brightener; and
  - (b) a silicone compound selected from the group consisting of high molecular weight dimethicones.
4. The hair care composition of claim 3 further comprising a carrier suitable for application to the hair.
- 20 5. The hair care composition of claim 4 wherein the optical brightener is a polystyrylstilbene.
6. The hair care composition of claim 1 or claim 3 containing from about 0.001 wt% to about 20 wt% of the optical brightener.
- 25 7. The hair care composition of claim 6 containing from about 0.01 wt% to about 15 wt% of the silicone compound.
8. The hair care composition of any of claims 1-7 further comprising a conditioning agent.
- 30 9. A shampoo composition comprising:
  - (a) an effective amount of an optical brightener;
  - (b) a detergentsurfactant suitable for cleansing the hair; and
  - (c) a silicone compound.
- 35 10. The shampoo composition of claim 9 further comprising a carrier suitable for application to the hair.

11. The shampoo composition of claim 10 wherein the optical brightener is selected from the group consisting of polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, 5 porphyrins, imidazoles, and mixtures thereof.
12. The shampoo composition of claim 11 containing from about 0.001 wt% to about 20 wt% of the optical brightener.
- 10 13. The shampoo composition of claim 12 containing from about 0.01 wt% to about 15 wt% of the silicone compound.
14. The shampoo composition of any of the preceding claims further comprising a conditioning agent.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 97/16412

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A61K7/13 A61K7/06

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 717 978 A (CURTIS HELENE IND INC) 26 June 1996 see page 21; claims 1,13,35; examples 35,72	3,4,6-14
X	GB 2 307 639 A (GEN ELECTRIC) 4 June 1997 cited in the application see page 8, line 3 – page 9, line 14; claims 1-9,11,12	1-4,6
E	EP 0 834 303 A (KAO CORP) 8 April 1998 see example 9	3,4,6-14
X	GB 1 328 108 A (UNILEVER LTD) 30 August 1973 cited in the application see page 1, line 65-92; claim 6	1,2
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means.
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

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**INTERNATIONAL SEARCH REPORT**

International Application No PCT/US 97/16412
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**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 733 355 A (KAO CORP) 25 September 1996 see example 2	3, 4, 6-14
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